

Structure and properties of radiation modified polyethylene

U V Ancharova^{1,3*}, M A Mikhailenko¹, M R Sharafutdinov¹, B P Tolochko¹,
K B Gerasimov¹, M V Korobeynikov^{2,3} and A A Bryazgin^{2,3}

¹Institute of Solid State Chemistry and Mechanochemistry SB RAS, Kutateladze, 18, 630128 Novosibirsk, Russia

²Budker Institute of Nuclear Physics SB RAS, Lavrentieva, 11, 630090 Novosibirsk, Russia

³Novosibirsk National State Research University, Pirogova, 2, 630090 Novosibirsk, Russia

E-mail: ancharova@gmail.com

Abstract. Polyethylene was irradiated with intensive electron beam with different doses. Structure changes after irradiation *ex situ* and *in situ* during heating up to its melting point were studied using synchrotron radiation X-Ray diffraction and thermal analysis.

1. Introduction

The intensive electron beam can modify structure and properties of inorganic and organic materials, crystal or amorphous. Ionizing radiation impact on polymer materials in different ways, such as introduction of defects into the crystal structure, breaking bonds in polymers, that in turn can lead to formation of other bonds in the structure and changes in mechanical or physical-chemical properties of polymer materials [1].

Polyethylene structure $-(\text{CH}_2\text{-CH}_2)_n-$ looks like zigzag chains of carbon atoms, each carbon atom of the chain is connected with two hydrogen atoms. Usually chains tend to form crystalline domains with amorphous surrounding. Polyethylene crystal structure [2] has orthorhombic symmetry with the space group Pnam (#62), with lattice parameters $a=7.41\text{\AA}$; $b=4.94\text{\AA}$; $c=2.55\text{\AA}$. Polymer chains extend along c -axis in the crystal and each unit cell consists of one formula unit $-(\text{CH}_2\text{-CH}_2)_n-$ and contain two perpendicularly zigzagged chains (see the Figure 1).

The irradiation causes two oppositely going processes in polymers – scissioning (cleavage) and crosslinking of the chains [3]. Crosslinking is the formation of a three-dimensional polymer network. In subjecting any polymer to electron beams or X-rays, the amount of energy input and multitude of hemolytic bond cleavages can result in either polymer chain extension and then crosslinking or polymer breakdown and scissioning.

The crosslinking prevails in polyethylene resulting in mechanical properties changing.

To understand the nature of polymer properties changing one ought to comprehend the changes in local structure after irradiation. The most direct way is to investigate the structure by X-ray diffraction method, especially synchrotron radiation XRD, as the X-Ray scattering on light elements is not intense enough. Thermal analysis helps to connect structure changes with changing in properties of polyethylene [4].



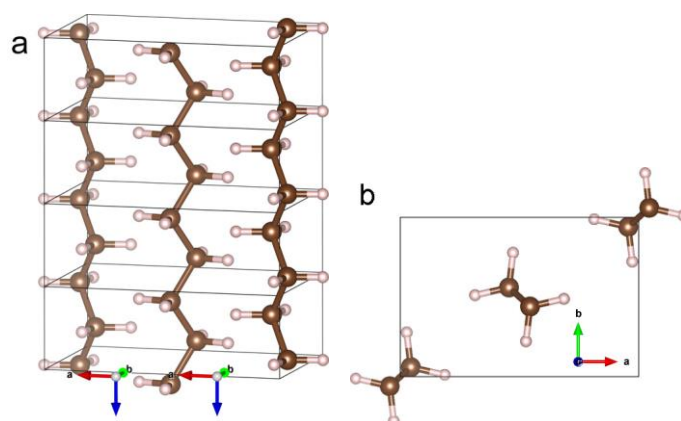


Figure 1. Polyethylene crystal structure (a) general view; (b) projection on (001) plane.

2. Experiment

LDPE - Low Density Polyethylene samples having thicknesses of ~ 1 mm were tested. The samples were subjected to electron beam treatment with doses of 2, 4, 6, 8, 16 and 40 kGy at room ambient conditions (temperature and pressure). The electron beam was generated by ILU-6 electron accelerator (located in BINP SB RAS, Novosibirsk, Russia), beam parameters were as follows: electron energy of 2.4 MeV, pulse beam current of 320 mA, pulse duration of 0.6 ms, pulse repetition rate of 2 Hz, underbeam transportation velocity of 2 cm/s. The absorbed dose was determined by number of underbeam passages, during one passage sample got the dose 2 kGy during approximately 4-5 seconds under beam window. The samples temperature was kept below 35°C to avoid structural changes caused by temperature increase. Time between passages during radiation treatment was not less than 30-40 seconds.

Ex situ investigations of polymers structure changes in XRD experiments were carried out at the experimental station on the 4th beamline of VEPP-3 storage ring in BINP SB RAS. X-rays had a wavelength of 0.3685 \AA . In situ investigations during heating of polyethylene have been made at 5b SR experimental station of VEPP-3 storage ring, $\lambda = 1.516 \text{ \AA}$. Heating has been made in opened furnace at air up to the temperature of polyethylene melting point $\sim 120^{\circ}\text{C}$.

Samples for thermal analysis were prepared as follows. For calorimetric investigations round tablets with diameter 3 mm were cut of the plates of polyethylene. To remove residual stresses in material after that process they were annealed at 70°C during 2 hours. After that samples were irradiated at the same conditions as that for XRD investigations.

Calorimetric investigations were carried out with using DSC 200F3 (NETZSCH) calorimeter in sealed crucibles in the temperature range from -160°C to 140°C with a heating rate of $10^{\circ}\text{C}/\text{min}$.

3. Results and discussion

Initial polyethylene samples and samples were irradiated by electron beam with doses of 2, 4, 6, 8, 16 and 40 kGy and then were investigated in the bulk state by synchrotron radiation X-ray diffraction method. Figure 2 shows resulting XRD patterns, demonstrating certain changes in polyethylene crystalline structure after irradiation. One can see that for initial state width of peaks were significantly higher than for irradiated samples, it points to increase in crystalline degree (size of domains and/or perfection in crystallite structure). It can be seen that the positions of the peaks tend to change for some peaks: they shift in different directions depending on crystallographic indexes. It means that crystal structure changes: the XRD analysis shows that the crystalline lattice expands along a and b axes and shrinks along c axis (see Figure 1a). That phenomenon can be connected with polymer cross-linking in transversal direction of the main chains in crystal, that also can cause changes in mechanical properties after irradiation, because cross-linking takes place not only in crystalline (visible in XRD) but also in amorphous part of the material.

Structure changing in polyethylene (PE) during heating up to melting point were studied. The irradiated and initial samples were heated up to 120°C with a rate of 5°C/min and their XRD were investigated in continuous mode with a frame rate of one frame per second. The changes in position and width of the (110) peak for PE during heating after irradiation with different doses are presented in Figure 3.

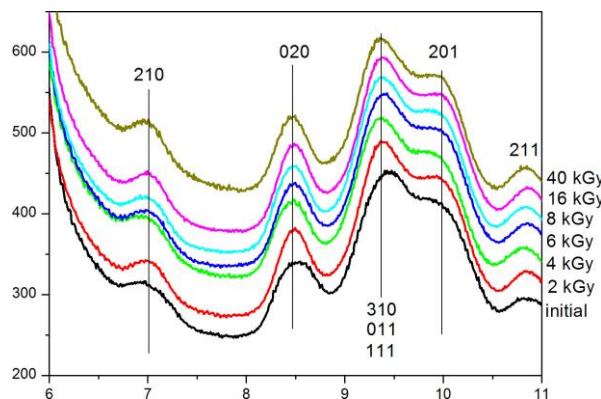


Figure 2. XRD scattering intensity $I(2\theta)$ in arbitrary units for polyethylene after irradiation with high energy electrons of different doses (0-40 kGy); $\lambda=0.3685\text{\AA}$.

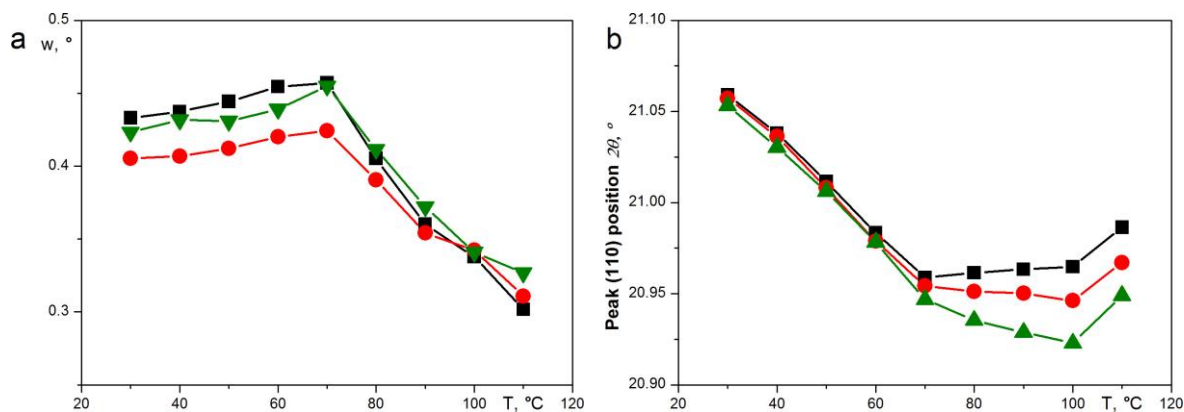


Figure 3. Changes in (a) widths; (b) positions of (110) XRD reflection of PE during heating of irradiated polyethylene after irradiation with doses 0 kGy (■), 4 kGy (●), 40 kGy (▲), $\lambda=1.516\text{\AA}$.

Widths of (000) peak (small angle scattering) for any considered irradiation doses gradually increase and reach maximum at the temperature of 100°C right before the melting point of PE and then gradually decrease, while widths of (110) peak also gradually increase to the point 70°C and then gradually drop down (fig. 3a). At the same temperatures the tendency in changes of peak position (fig. 3b) changes: below 70°C it gradually decrease, then behavior for different doses differs but in general does not change and after 100°C tends to increasing. Changes in intensity of (110) peak depending on temperature (fig. 5a) also correlate. *That means that that temperatures are singular points in changes in structure and properties of PE.* Probably the first of them is connected to the temperature of activation of collective oscillations in chain, that can initiate changes in structure: the process of crosslinking in crystalline fraction of polymer; and the second one is the temperature of pre-melting. Main differences for samples irradiated with different dozes are observed in a final peak position, it has the lower values the higher was irradiation doze (fig. 3b). It means that after irradiation structure of PE becomes to be more loose and stretched along transversal directions towards polymer chains.

Figure 4 shows thermoanalysis results for irradiated and initial polyethylene samples.

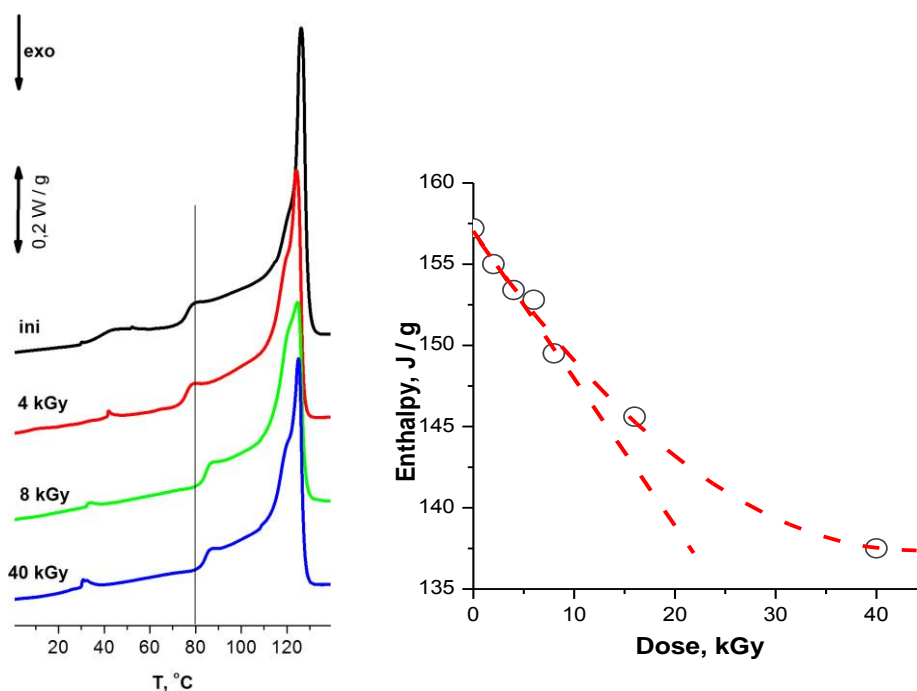


Figure 4. (left) absorbed energy during heating of irradiated polyethylene having doses from top to bottom: 0; 4; 8; 40 kGy; (right) thermal effect depending on irradiation dose.

The most part of energy absorbed by the material during irradiation with low doses is to increase the internal energy of the sample and the variation of heat can be described by a linear dependence $Y=157.1-0.88X$ by points below 10 kGy. During calculations with using points above 10 kGy the dependence of the thermal effect on the absorbed dose of ionizing radiation can be described by the second-order polynomial $Y=156.96-0.89X+0.01016X^2$, here X is the irradiation dose. Thermal effects were calculated using a sigmoidal baseline from 0 to 150°C using Proteus Analysis software.

The values of melting points change without any clear dependence and lay in the range of 124-127°C. It disappears the pronounced thermal effect of low-temperature softening at 45°C (existing for initial sample), which is usually referred by properties to amorphous phase of polyethylene. Also it changes the temperature of viscous fluid transition (plastic) appearing at 75°C for initial sample, which can be referred by properties to the ordered phase of polyethylene. Thermal effects of glass transition unfortunately failed to be reliably obtained.

Obviously at the beginning stage of irradiation it occurs mostly transformations of not ordered part of PE. As mobility of their chains allows to achieve the maximal efficiency of irradiation. Then after crosslinking the mobility of polymer network of not-ordered fraction approach to that for ordered part of polyethylene and efficiency of irradiation drops down.

4. Conclusion

Structure investigation show that polyethylene after irradiation tend to form more 'loosening' structure, it points on creating bonds during crosslinking in transversal to chains direction, that affect also the crystal structure properties and changes in lattice parameters. Comparing XRD and thermoanalysis results one can conclude that the singular point of ~70-75 °C can be connected to crosslinking of ordered fraction of PE, occurring during heating of the sample as a result of increasing mobility in chain network.

The described XRD method is rather fast not nondestructive analysis method and can be used for gel fraction estimation and measurement.

5. Acknowledgement

X-ray diffraction experiments were carried out with involvement of equipment belonging to the shared research center SSTRC, BINP SB RAS.

References

- [1] Forgács P, Tolochko B P, Sheromov M A 1981 *Polymer Bulletin* **6** 127
- [2] Bunn C W 1945 *Chemical Crystallography*, Oxford University Press 233
- [3] Industrial radiation Processing With Electron beams and X-rays 201. International Atomic energy Agency technical document, <http://www.cirms.org/pdf/Industrial%20Radiation%20Processing%20-%20May%202011%20-%20Revision%206.pdf>
- [4] Minkova L, Nikolova M, Nedkov E 1988 *Journal of Macromolecular Science B: Physics* **1** 99